Patent Specification
Applicants: Zhong Xu
Robert M. Conforti
William M. Risen, Jr.
Assignee: Arkwright, Inc.
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INK-JET MEDIA HAVING IMPROVED WATER FASTNESS

CROSS-REFERENCE TO RELATED APPLICATIONS

[01] This application claims the benefit of U. S. Provisional Application No. 60/430,218 having a filing date of December 2, 2002, the entire contents of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[02] The present invention generally relates to imaging media suitable for use with narrow and wide format ink-jet color printers. Particularly, the invention relates to ink-jet recording media comprising a substrate material coated with an ink-receptive layer comprising a polymer film-forming binder and certain dye fixative particles. The media can be used to produce images having high color quality and good water-fastness.

[03] In recent years, the market for ink-jet color prints having good water-fastness properties has grown. The ink-jet industry is constantly looking to develop new ink-jet media that will accept and hold the ink when the printed media is exposed to water and other liquids. These properties are important for ink-jet media used in indoor applications such as media used to record digital photographs, and media used to make greeting cards, calendars, invitations, announcements, leaflets, and the like. Good water-fastness properties are also

important for media used in outdoor applications such as outdoor signs, posters, advertising banners, and other display graphics. Narrow and wide format color ink-jet printers are used to produce such imaged media products depending upon the size of the media and intended end-use application.

[04] Generally, in an ink-jet printing process, liquid ink is squirted through very fine nozzles in a printer to form an image (print) directly on a recording medium. Typically, the ink-jet recording medium is a film or paper substrate coated with a specially designed ink-receiving coating. The quality of the final image is partly dependent upon the structure of the ink-jet recording medium particularly the coating composition and substrate material.

[05] The inks used in most ink-jet printers are aqueous-based inks containing molecular dyes and/or pigmented colorants. Water is the major component in aqueous-based inks and small amounts of water-miscible solvents such as glycols and glycol ethers also may be present. Other ink-jet inks used in the industry are non-aqueous based inks containing organic vehicles. During the printing step, dyes or colorants from the ink can penetrate into the ink-receptive coating on the medium. Water and other solvents can evaporate from the printed medium as the medium is dried. By "ink-receptive coating" or "ink-receptive layer" as used herein, it is meant a coating or layer that is capable of receiving (absorbing) at least aqueous-based inks. The ink-receptive coating or layer may also receive non-aqueous based inks in some instances.

[06] In the past, many approaches have been employed to develop ink-jet media capable of recording images having high color brilliance, fidelity, sharpness, and water-fastness as well as other desirable properties. Although some conventional ink-jet media may be effective in some instances in producing such color images, there is a need for an improved ink-jet recording medium. The present invention provides such a medium. These and other objects, features, and advantages of this invention are evident from the following description.

SUMMARY OF THE INVENTION

[07] The present invention relates to an ink-jet recording medium, comprising a base substrate having a surface coated with an ink-receptive layer comprising at least 5 % by weight of a polymer film-forming binder and at least 5 % by weight of dye fixative particles based on total dry weight of the ink-receptive layer. The base substrate can be any suitable material such as a paper or film. Papers having a glossy surface finish can be used. The dye fixative particles have novel dye fixative properties and are selected from the group consisting of silica particles with pendant polyvinylamine, silica particles with pendant polyethyleneimine, silica particles with pendant trimethylammonium chloride, silica particles with pendant pyridine groups, and polystyrene particles with pendant piperidinomethyl groups.

[08] The ink-receptive layer may further comprise a non-polymeric organic metal complex such as an amine complex containing zirconium. Other additives such as ultraviolet light stabilizers may be included in the ink-receptive layer.

DETAILED DESCRIPTION OF THE INVENTION

[09] The present invention relates to an ink-jet recording medium comprising a substrate material coated with an ink-receptive composition comprising a film-forming binder and certain particles having novel dye fixative properties (hereinafter referred to as novel dye fixative particles or "NDFP").

[10] The ink-jet recording media of the present invention are constructed using a suitable substrate material. For example, the substrate may be a paper material. Paper substrates are known in the ink-jet industry and any suitable paper may be used in the present invention. For example, plain papers, clay-coated papers, or polyolefin-coated papers may be used. The paper substrate may have different surface finishes. For instance, glossy paper substrates, wherein the substrate has a relatively high surface gloss may be used. In other embodiments, satin-like or semi-glossy substrates may be used. In still other embodiments, matte-like substrates may be used.

[11] Alternatively, the substrate may be a polymeric film comprising a polymer, such as, polyethylene, polypropylene, polyester, naphthalate, polycarbonates, polysulfone, polyether sulfone, poly(arylene sulfone), cellulose triacetate, cellophane, polyvinyl chloride, polyvinyl fluoride, polyimide, polyesters, polystyrene, polyacrylics, polyacetals, ionomers, and mixtures thereof. In other instances, a metal foil such as aluminum foil or a metal-coated material can be used as the substrate.

[12] The substrate material has two surfaces. The first surface, which is coated with the ink-receptive layer or layers in accordance with this invention, may be referred to as the "front" or "imaging" surface. The second surface, which is opposite to the first surface, may be referred to as the "back" or "non-imaging" surface.

[13] The substrate material is coated with an ink-receptive composition in accordance with the present invention to produce an ink-receptive layer. The ink-receptive layer comprises about 5% to about 95% by weight polymer film-forming binder and about 95% to about 5% by weight novel dye fixative particles based on total dry weight of the ink-receptive layer. The resulting ink-receptive layer has a porous film-like structure with good cohesiveness and mechanical strength.

[14] Suitable polymer film-forming binders include, for example, those selected from the group consisting of polyvinyl alcohols; modified polyvinyl alcohols (e.g., carboxyl-modified PVA, silicone-modified PVA, maleic acid-modified PVA, and itaconic acid-modified PVA); poly(vinyl pyrrolidone); vinyl pyrrolidone copolymers; poly(2-ethyl-2-oxazoline); poly(ethylene oxide); poly(ethylene glycol); poly(acrylic acids); starch; modified starch (e.g., oxidized starch, cationic starch, hydroxypropyl starch, and hydroxyethyl starch), cellulose; cellulose derivatives (e.g., oxidized cellulose, cellulose ethers, cellulose esters, methyl cellulose, hydroxyethyl cellulose, carboxymethyl-cellulose, benzyl cellulose, phenyl cellulose, hydroxypropyl cellulose, ethyl hydroxyethyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl methyl cellulose, hydroxy butylmethyl cellulose, dihydroxypropyl cellulose,

hydroxypropyl hydroxyethyl cellulose, chlorodeoxycellulose, aminodeoxycellulose, diethylammonium chloride hydroxyethyl cellulose, hydroxypropyl trimethyl ammonium chloride hydroxyethyl cellulose; polyamides; alginates and water-soluble gums; dextrans; carrageenan; xanthan; chitin; proteins; gelatins; agar; and mixtures thereof.

[15] In one embodiment, a water-insoluble binder such as a polyamide resin is used as the film-forming binder. The ink-receptive layer of this invention further includes novel dye fixative particles (NDFP) as described in further detail below.

[16] A. Inorganic NDFP

[17] The following inorganic NDFP can be used in the ink-receptive layer: i) silica particles with pendant polyvinylamine, and ii) silica particles with pendant polyethyleneimine. These particle materials currently are available as CuWram products from Purity Systems, Inc. (Missoula, MT) and are available in an initial particle size of about 165 – 200 mesh, so that particles of about 75 microns are readily available. Grinding of the particles may be necessary depending on the intended media application and coating smoothness requirement. Alternatively, such NDFP can be produced with smaller silica particles to obtain particles in the 0.05 to 75 μm range. These particles currently are produced and sold for a variety of non media applications, such as metal ion recovery, chemical catalysis, etc., but the inventors have discovered that they can be used in combination with a polymer binder to form an ink-receptive layer having desirable properties.

[18] Also, trimethylammonium chloride propylsilicate particles designed and used for chemical separations in the chemical analysis and pharmaceutical synthesis areas (available from Silicycle, Inc., Quebec City, Canada as "Si-TMA Chloride) can be used in the ink-receptive layer.

[19] Additional compositions that are appropriate for achieving the water-fastness include particles based on alumina with attached dye-mordanting

functional groups, other than OH groups, such as those based on amine, quaternized amine, pyrridinium, or pyrrolidone types.

[20] Additional compositions that are useful for achieving the water-fastness include silica-, alumina-, and/or titania-based particles that are attached to polymeric molecules that can comprise the matrix of the ink jet-receptive film. Still other compositions of this type are characterized further by having the inorganic or polymeric molecules comprise amine or quaternary amine mordanting groups. Examples of the compositions of these types include silica-based particles that are reacted first with aminoalkyltriethoxysilane molecules and then subsequently with a less than stoichiometric (NCO to NH_2) amount of isocyanate-terminated oligomers or polymers to form a NDFP attached to a polymer or polymeric composite that comprises the matrix material when used in an ink jet-receiving film. Other examples include silica-based particles with pendant mordant groups based on pyridine, pyridinium, polyvinylpyridine or polyvinylpyrrolidone.

[21] A range of NDFP materials can be synthesized within this invention which have inorganic particles with attached polymeric or non-polymeric dye-mordanting functionalities.

[22] B. Non-Polymeric Organic Metal Complexes

[23] In addition to the above-described NDFP and polymer film-forming binders, the ink-receptive layer may contain organic metal complexes. Organic metal complexes have been widely used as adhesion promoters for many industry coatings on plastic or metal surfaces. It has been found that these organic metal complexes can fix ink-jet dyes effectively. One example of such an organic metal complex is Chartwell B-515.1, available from Chartwell International, Inc. (North Attleboro, MA), which is a bimetallic amine complex containing the metal zirconium.

[24] C. Other Additives

[25] Also, the ink-receptive layer of this invention may contain additional dye-fixative additives such as an inorganic metal complex. For example, an aluminum chlorohydrol solution available from Grace Davison (Columbia, MD) as Sylojet A200 can be used. The chemical structure of Sylojet A200 is $Al_2(OH)_5Cl$. Also, an amine-functionalized silica aerogel with a functionality of at least 0.7 mmol amine per gram of a silica aerogel with an initial surface area of at least 250 m^2/g can be used. This aerogel material is available from Industrial Science and Technology Network, Inc.

[26] The ink-receptive layer may further contain additives such as inorganic and organic pigments, plasticizers, surface active agents that control the wetting or flow behavior of the coating solutions, antistatic agents, suspending agents, antifoam agents, acidic compounds to control pH, optical brighteners, ultraviolet light (UV) blockers/stabilizers, and the like. In cases where UV stability is required, it particularly is contemplated that alumina-containing particles can be added to the ink-receptive layer.

[27] The ink-receptive coating is applied to the front surface of the substrate using conventional methods to form an uniform ink-receptive layer. Suitable methods for coating the base substrate with the ink-receptive coating include, for example, Meyer-rod, slot-die, roller, blade, wire bar, dip, solution extrusion, reverse roll, air-knife, curtain slide, doctor-knife, and gravure methods. The slot-die and Meyer-rod methods are preferred because of their ease of use. Then, the coating is dried using forced hot air ovens or other suitable drying methods. It is also recognized that the base substrate may be coated with multiple ink-receptive layers. For example, in some instances, it may be desirable to include one or more under layers or primer coatings between the substrate and above-described ink-receptive layer. Also, it may be desirable to coat top ink-receptive or protective layers over the above-described ink-receptive layer.

[28] The ink-receptive coatings of this invention provide good ink absorption layers when applied to the substrate. As discussed above, the particles in the ink-receptive layer can have functional groups attached to them to help absorb

the ink dyes or pigments. Furthermore, the particles and film-forming binder form a porous coating structure that efficiently absorbs water or other ink solvents. The particles have a high surface area and form interstitial pores or voids that are effective in wicking and retaining the ink. A conventional ink-jet printer can be used to print an image onto the ink-receptive coating. When the ink is impinged on the coating, it can enter the interstitial voids and spaces in the coating structure. The film-forming binder holds the particles in place and provides cohesion to the layer and does not detrimentally affect the porosity of the layer.

[29] The resulting ink-jet recording media can be imaged by narrow and wide format ink-jet printers with aqueous or pigmented color inks to provide printed images having dense and bright colors, high color sharpness, and good water-fastness. Particularly, the ink-jet recording media of this invention are characterized by having a percentage loss of color optical density of less than about 20% as demonstrated in the Examples below.

[30] The present invention is further illustrated by the following examples using the below-described test methods, but these examples should not be construed as limiting the scope of the invention.

[31] **<u>Test Methods</u>**

[32] **<u>Water-Fastness</u>**

[33] Ink jet image colors fade under exposure to water. A commonly used method for measuring color is the color optical density. In order to quantitatively measure the water-fastness, optical density values of red, green, blue, cyan, magenta, yellow and composite black colors are measured before and after the samples are washed with water. The sum of the optical densities of these colors is used to characterize the overall color vibrancy. Percentage loss of optical density is a measure of the color difference between the washed and unwashed imaged samples. Samples and colors having poor water-fastness have larger percentage loss values. The values of optical density were measured with a X-Rite 408 Colorimeter (X-Rite, Inc.)

[34] The samples were printed with multicolor test patterns using an HP 970CSE desktop ink-jet printer in a "photo paper" mode. The water-fastness of the imaged samples was determined by exposing the samples to flowing water over a period of 10 minutes under the room temperature. The optical density values of the samples were measured before and after being washed with water. The percentage loss of optical density of the samples was calculated as described above.

[35] **Examples**

[36] **Example 1**

In this Example 1, the following coating formulation was prepared. The weight percentages of the components in the coating are approximate weights based on total weight of the coating formulation.

Ink-Receptive Coating	
Water	28%
Ethanol	47%
Elvamide 8023 [1]	5%
Orgasol 3501 [2]	17.5%
VP-1 [3]	2.5%

1. Polyamide binder resin, available from DuPont (Wilmington, Delaware).
2. Polymeric particles of a polyamide, available from Elf Atochem North America.
3. Silica particles with pendant polyvinylamine, Purity Systems, Inc. (Missoula, MT).

The above-described ink-receptive coating was applied to a base substrate as further described below. The resulting ink-receptive layer contained about 70 weight percent of polyamide particles (Orgasol 3501) and 10 weight percent of silica particles with pendant polyvinylamine (VP-1); and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[37] **Example 2**

In this Example 2, the following coating formulation was prepared.

Ink-Receptive Coating	
Water	28%
Ethanol	47%
Elvamide 8023	5%
Orgasol 3501	17.5%
Derivatized Silica Gel, TMA Chloride [4]	2.5%

4. Silica particles with pendant trimethylammonium chloride, Silicycle, Inc. (Quebec, Canada).

[38] The above-described ink-receptive coating was applied to a base substrate as further described below. The resulting ink-receptive layer contained about 70 weight percent of polyamide particles (Orgasol 3501) and 10 weight percent of silica particles with pendant trimethylammonium chloride (Derivatized Silica Gel, TMA Chloride); and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[39] **Example 3**

In this Example 3, the following coating formulation was prepared.

Ink-Receptive Coating	
Water	28%
Ethanol	47%
Elvamide 8023	5%
Orgasol 3501	17.5%
Derivatized Silica Gel, Pyridine-2 [5]	2.5%

4. Silica particles with pendant pyridine, Silicycle, Inc. (Quebec, Canada).

[40] The above-described ink-receptive coatings were applied to a base substrate as further described below. The resulting ink-receptive layer contained about 70 weight percent of polyamide particles (Orgasol 3501) and 10 weight percent of

silica particles with pendant pyridine group (Derivatized Silica Gel, Pyridine-2); and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[41] **Example 4**

In this Example 4, the following coating formulation was prepared.

Ink-Receptive Coating	
Water	28%
Ethanol	47%
Elvamide 8023	5%
Orgasol 3501	17.5%
Piperidinomethyl Resin [6]	2.5%

6. Polystyrene particles with pendant piperidinomethyl group, Glycopep Chemicals, Inc. (Chicago, IL).

[42] The above-described ink-receptive coatings were applied to a base substrate as further described below. The resulting ink-receptive layer contained about 70 weight percent of polyamide particles (Orgasol 3501) and 10 weight percent of polystyrene particles with pendant piperidinomethyl group (Piperidinomethyl Resin); and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[43] **Prophetic Example**

In this Example, the following coating formulation could be prepared.

Ink-Receptive Coating	
Water	28%
Ethanol	47%
Elvamide 8023 [1]	5%
VP-1 [2]	20%

1. Polyamide binder resin, available from DuPont (Wilmington, Delaware).
2. Silica particles with pendant polyvinylamine, Purity Systems, Inc. (Missoula, MT).

[44] The above-described ink-receptive coating could be applied to a base substrate as described below. The resulting ink-receptive layer would contain about 80 weight percent of silica particles with pendant polyvinylamine (VP-1) and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[45] **Comparative Example A**

In this Comparative Example A, the following coating formulation was prepared.

Ink-Receptive Coating	
Water	28%
Ethanol	47%
Elvamide 8023	5%
Orgasol 3501	17.5%
Gasil IJ-35 [7]	2.5%

7. Silica gel particles, Ineos Silicas Americas LLC (Joliet, IL) .

[46] The above-described ink-receptive coating was applied to a base substrate as further described below. The resulting ink-receptive layer contained about 70 weight percent of polyamide particles (Orgasol 3501) and 10 weight percent of regular silica gel particles (Gasil IJ-35); and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[47] **Comparative Example B**

In this Comparative Example B, the following coating formulation was prepared.

Ink-Receptive Coating	
Water	28%

Ethanol	47%
Elvamide 8023	5%
Orgasol 3501	17.5%
Luvicross M [8]	2.5%

8. Crosslinked polyvinylpyrrolidone particle, BASF (Mount Olive, NJ).

[48] The above-described ink-receptive coating was applied to a base substrate as further described below. The resulting ink-receptive layer contained about 70 weight percent of polyamide particles (Orgasol 3501) and 10 weight percent of crosslinked polyvinylpyrrolidone particle (Luvicross M); and about 20 weight percent of a water-insoluble polymeric binder (Elvamide 8023) based on total dry weight of the ink-receptive layer.

[49] In above examples, the ink-receptive coating was applied to a polyethylene-coated paper substrate using a Meyer metering rod and dried in an oven at 110 °C for about 2 minutes. The dry weight of the ink-receptive coating was about 20 gsm. Per the Test Methods described above, images (prints) were produced on the coated ink-jet recording media, and the images were evaluated for water-fastness. The results are reported below in Table I.

[50] TABLE I

ID	Type of surface modified particles	Percentage Loss of Color Optical Density
Example 1	silica particles with pendant polyvinylamine (VP-1)	1%
Example 2	silica particles with pendant trimethylammonium chloride (Derivatized Silica Gel, TMA Chloride)	5%
Example 3	Silica particles with pendant pyridine group (Derivatized Silica Gel, Pyridine-2)	13%
Example 4	Polystyrene particles with pendant piperidinomethyl group (Piperidinomethyl Resin)	16%
Comparative Example A	Silica gel particles (Gasil IJ-35)	24%
Comparative Example B	Crosslinked polyvinylpyrrolidone particles (Luvicross M)	24%

[51] It is appreciated by those skilled in the art that various changes and modifications can be made to the description and illustrated embodiments herein without departing from the spirit of the present invention. All such changes and modifications are intended to be covered by the appended claims.